WIDE RANGE ANALYSIS OF OZONE GAS CONCENTRATION IN ULTRAVIOLET REGION

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Specially dedicated to my beloved parents, Yaacob and Hamidah; my husband, Ahmad Muhaimin and my son, Abdullah Muhammad for their prayers, patience and support

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ABSTRACT

The purpose of this research is to investigate the development of optical gas sensor employing absorption spectroscopy technique for ozone concentration measurement. Additionally, wide range analysis has been conducted to improve range of ozone concentration measurement using ultraviolet light absorption. Simulation of ozone absorption cross section in ultraviolet region was conducted via Spectralcalc.com® simulator. Simulation result for ozone absorption cross section was then verified by comparison with result from previous studies, showing small percentage of difference less than 3.05 %. In addition, the simulator was also used to investigate the effect of pressure and temperature on ozone absorption cross section. Simulation result showed ozone absorption cross section to exhibit negligible effect of pressure and temperature from 0.1 atm until 2.0 atm and from 293 K until 305 K, respectively. Next, path length of gas cell that suits with detection range of ozone monitor was determined through Spectralcalc.com® simulator. Finally, transmissive type gas cell is fabricated at optimum length of 10 cm. Based on the experiment results wide range analysis was conducted at 10 cm gas cell by consideration of less relative error of concentration. It was observed that wavelengths at 232 nm, 233 nm, 234 nm, 235 nm, 236 nm, 284 nm, 285 nm, 286 nm and 287 nm exhibit capability to measure ozone concentration using ultraviolet light absorption at high concentration value with wide range of concentration measurement from 619 ppm until 932 ppm. Of this, 285 nm was chosen due to its high resolution value at 17 ppm. The sensor exhibits fast response time and recovery time, both at 20 s. Peak of ozone absorption cross sections were observed in both experiment and simulation, located at 260.45 nm and 255.44 nm, respectively. Meanwhile, the values of peak of ozone absorption cross section were observed in experiment and simulation at 164.37×10^{-23} m^2 $molecule^{-1}$ and 114.86×10^{-23} m^2 $molecule^{-1}$, respectively. Significantly, this research has successfully demonstrated possibility of conducting wide-range analysis employing consideration of less relative error concentration. Particularly, vast improvement range of ozone concentration measurement has been achieved by wavelength selection which is far from the peak of ozone absorption cross section.

ABSTRAK

Tujuan penyelidikan ini adalah untuk mengkaji pembangunan penderia gas optik berdasarkan teknik spektroskopi penyerapan untuk mengukur kepekatan ozon. Selanjutnya analisis perluasan julat telah dijalankan bagi memperbaiki julat pengukuran kepekatan ozon menggunakan penyerapan cahaya ultraungu. Simulasi keratan rentas penyerapan ozon di rantau ultraungu dijalankan melalui penyelaku Spectralcalc.com®. Keputusan simulasi bagi keratan rentas penyerapan ozon kemudiannya disahkan melaui perbandingan dengan kajian terdahulu. Keputusan menunjukkan peratusan perbezaan yang kecil, kurang daripada 3.05%. Penyelaku ini juga digunakan untuk mengkaji kesan tekanan dan suhu terhadap keratan rentas penyerapan ozon. Keputusan simulasi menunjukkan kesan tekanan dan suhu terhadap keratan rentas penyerapan ozon boleh diabaikan, masing-masing dari 0.1 atm sehingga 2.0 atm dan dari 293 K hingga 305 K. Seterusnya, panjang sel gas yang dapat mengukur julat kepekatan ozon sepadan dengan alat pengukur ozon ditentukan melalui penyelaku Spectralcalc.com®. Sel gas jenis *transmissive* difabrikasi pada panjang optimum 10 cm. Berdasarkan keputusan eksperimen, analisis perluasan julat dijalankan pada sel gas 10 cm dengan pertimbangan nilai ralat relatif kepekatan yang kecil. Didapati bahawa panjang gelombang 232 nm, 233 nm, 234 nm, 235 nm, 236 nm, 284 nm, 285 nm, 286 nm dan 287 nm menunjukkan keupayaan mengukur kepekatan ozon menggunakan penyerapan cahaya ultraungu pada nilai kepekatan Panjang gelombang 285 nm dipilih kerana nilai resolusinya yang tinggi pada 17 ppm. Penderia ini mempamerkan masa tindak balas dan masa pemulihan yang pantas, masing-masing pada 20 s. Puncak keratan rentas penyerapan ozon diperhatikan daripada keputusan eksperimen dan simulasi masing-masing terletak pada 260.45 nm dan 255.44 nm. Manakala, nilai puncak keratan rentas penyerapan ozon daripada keputusan eksperimen dan simulasi masing-masing adalah 164.37×10^{-23} $m^2molekul^{-1}$ dan 114.86×10^{-23} $m^2molekul^{-1}$. Kajian ini telah berjaya menunjukkan kemungkinan menjalankan analisis perluasan julat berdasarkan pertimbangan nilai kepekatan ralat relatif yang kecil. Julat pengukuran kepekatan ozon berdasarkan penyerapan cahaya ultraungu telah ditambahbaik dengan pemilihan panjang gelombang yang terletak jauh dari puncak keratan rentas penyerapan ozon.

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LIST OF ABBREVIATIONS

Ag_2WO_4	-	Silver Tungstate
AOT40	-	Accumulated exposure of ozone concentration over a threshold of 40 ppbv
Au/TiO_2-WO_3	-	Gold//Titanium dioxide-Tungsten Trioxide
CCD	-	Charge Coupled Devices
$CuAlO_2$	-	Copper Aluminium Oxide
e.s.r	-	Electron spin resonance
FUV	-	Far ultraviolet
HC	-	Hydrocarbon
HITRAN	-	High resolution transmission
In_2O_3	-	Indium oxide
KI	-	Potassium iodide
LED	-	Light Emitting Diodes
MUV	-	Middle ultraviolet
MV	-	Medium voltage
n.m.r	-	Nuclear magnetic resonance
NASA	-	National Aeronautics and Space Administration
NO_2	-	Nitrogen Dioxide
NO_x	-	Oxide of Nitrogen
NUV	-	Near ultraviolet
O_2	-	Oxygen
O_3	-	Ozone
PAN	-	Peroxyacetyl nitrates
PDA	-	Photodiode array
$PEO/RbI/I_2$	-	Polyethylene oxide/RubidiumIodide/Iodine
PMMA	-	Polymethylmethacrylate
ppb	-	Part per billion

ppm	-	Part per million
Pt/TiO_2-WO_3	-	Platinum/Titanium dioxide-Tungsten Trioxide
PTFE	-	Polytetrafluoroethylene
SIG	-	Southern Industrial Gas
SnO_2	-	Tin dioxide
UV	-	Ultraviolet
VOC	-	Volatile organic compounds
VUV	-	Vacuum ultraviolet
WO_3	-	Tungsten oxide
ZnO	-	Zinc Oxide

LIST OF SYMBOLS

A	-	Absorbance
$c_{(ppm)}$	-	Concentration of gas in ppm
c	-	Speed of light, 3×10^8 m s^{-1}
$c_{(molm-3)}$	-	Concentration in mol m^{-3}
dI	-	Amount of light absorbed in dl
dl	-	Thickness of an infinitesimally thin slab of sample
E	-	Photon energy in Joules (J)
f	-	Frequency (s^{-1} or Hertz)
h	-	Planck's constant, 6.63 x 10-34 J s
I	-	Intensity after the light passed through the sample
I_o	-	Intensities before the light passed through the sample
$\left(\frac{n}{V}\right)$	-	Concentration
$\left(\frac{I}{I_0}\right)$	-	Transmittance, (Tr)
l	-	Path length in m
n	-	Amount of substances in mol
N_A	-	Avogadro number, 6.022×10^{23} molecule mol^{-1}
P	-	Pressure of gas in atm
R	-	Gas constant, 8.205746×10^{-5} atm m^3 mol^{-1} K^{-1}
T	-	Temperature in K
Tr	-	Transmittance
V	-	Volume of gas in m^3
w	-	Wavenumber (cm^{-1})
$\Delta c / c$	-	Relative error of concentration (%)
ΔTr	-	Absolute error of transmittance
ε	-	Absorptivity in m^2 mol^{-1}

λ	-	Wavelength
ρ	-	Ozone density, 2.144 kg m^{-3}
σ	-	Absorption cross section of sample in m^2 $molecule^{-1}$
σ_s	-	Absorption cross section obtained in simulation work
ω	-	Molar mass of ozone, 48 $\times 10^{-3}$ kg mol^{-1}

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CHAPTER 1

INTRODUCTION

1.1 Background of Research

In 1785, ozone was discovered by Dutch scientist Martinus van Marum from observation on air exposed to electrical spark had characteristic smell and demonstrated redox properties. Later, the Swiss researcher Christian Schonbein in 1840 explained this phenomenon as formation of a special gas. In 1865, J.L. Soret named it ozone when this new gas was clearly identified as molecule containing three atom of oxygen. Ozone was named based on the Greek word "ozo'" which meant "smell".

Ozone is a gas of dark blue colour at normal temperature and pressure and dark-blue coloured liquid at temperature below -111.5 °C (Roshchina and Roshchina, 2003). It has pungent smell that can be detected by nose as sign of toxic gas. Chemical symbol for ozone is O_3 as formation of three atom of oxygen. Ozone has characteristic powerful oxidising property that is suitable for sterilization and bleaching. However, ozone is unstable and quickly reverts to oxygen.

Ozone can be produced by human or natural activity; therefore, ozone can be originated from many source. Naturally, thunder storm, ultraviolet irradiation of air and forest excretions are the main contributors to ozone generation (Roshchina and Roshchina, 2003). Meanwhile, increase in ozone level cause by human activity is due to waste from manufacturing industry (Leman *et al.*, 2010), indirect ozone discharge

from automobile exhaust (Park *et al.,* 2009) and any technology that produces ultraviolet irradiation such as photocopier, laser printer (Arshak *et al.,* 2007), and computer. Significant case study by Leman *et al.,* (2010) show ozone is one of the gas produced from welding process that is common in manufacturing industry. The case study was done in two car component manufacturer located in Shah Alam, Malaysia indicate ozone level varying from 0.001 until 0.13 ppm and 0.003 until 0.45 ppm for company A and company B, respectively.

Ozone is one of the gases that are naturally present in the atmosphere. It has both beneficial and damaging effects. At stratospheric layer, ozone plays significant role for life on Earth as it filters harmful ultraviolet radiation emitted by the Sun. However, when ozone is photochemically produced in the troposphere (at low altitudes and ground level), it can be toxic and results in significant physiological and ecological damage. Ozone may cause different kinds of serious health consequences such as irritation to the eyes, pulmonary oedema, and air passages, causing numerous respiratory problems (Arshak *et al,*. 2007), lung diseases and lung damage. The exposure limits for ozone gas can be found in Appendix A. In addition, study of the effect of ozone pollution associated with AOT40 (accumulated exposure of ozone concentration over a threshold of 40 ppbv) index is done in area of Ahmednagar, India. Measurement of ozone from January 2006 until December 2007 clearly revealed that winter wheat and summer crop yield reduction by 10% and 15%, respectively (Debaje *et al.,* 2010).

Chemical reaction between oxide of nitrogen (NO_x), which is emitted from various sources, including motor vehicles and other industrial sources, and hydrocarbon (HC) in presence of sunlight and oxygen (O_2) forms ground level ozone (O_3), and volatile organic compounds (VOC's) such as aldehydes and peroxyacetyl nitrates (PAN) (Dooly, 2008). These secondary pollutants form a noxious mixture of air known as photochemical smog have been identified as one of the primary pollutants that degrade air quality. Ground-level ozone forms easily in the atmosphere, normally in the warm urban atmosphere. There is study investigates the secondary pollutants resulting from household product use in presence of ozone. The use of trepenoid-cointaning cleaning products or air freshner combined with indoor

ozone produces substantial levels of secondary air pollutants specifically formaldehyde and fine particulate mass (Singer *et al.,* 2006).

Nevertheless, ozone also has the benefit due to its powerful oxidizing ability. Ozone is effective to eliminate colour, taste and odour. In addition, ozone destroys bacteria and viruses faster than other disinfection chemical. Hence, ozone is widely used for sanitization in drinking water treatment, wastewater treatment, odour control and air treatment (Buntat, 2010). Recently, the application of ozone is increasing in many fields including fruit juice preservation (Cullen *et al.,* 2010), food packaging (Naitou and Takahara, 2008), fabrication of semiconductor wafer, fish plant (Nakagawa *et al.,* 2001) and alternative insecticides for the control of insects and micro-organisms in stored products (Isikber and Athanassiou, 2015).

1.2 A Review on Ozone Sensor

With increasing use of ozone, there is a large demand to develop gas sensor for ozone monitoring system and detection. In the past couple of years, there are several type of gas sensor have been developed to determine ozone concentration including electrochemical, metal oxide semiconductor, optical sensor based on absorption in ultraviolet/visible region, carbon nanotube and reaction between ozone and dye or Potassium Iodide (KI). Table 1.1 summarized type of ozone gas sensor and its performance in term of range of ozone concentration measurement and response time.

Ozone gas sensor that is based on reaction between ozone and indigo carmine or azo dye orange I have advantages in term of simplicity, light, portable and passive device (Maruo, 2007 and Maruo *et al.,* 2010). Results of this reaction is colour-fading of indigo carmine or azo dye orange I due to presence of ozone. However, long response time is needed by this type of sensor for colour-fading reaction. In addition, carbon nanotube based sensor also exhibits the limitation of long response time (Park *et al.,* 2009).

Work by Stergiou *et al.*, (2010) demonstrates a proof-of concept for pH-metric determination of ozone in an unbuffered potassium iodide (KI) solution. The pH increase due to the reaction of ozone with an unbuffered KI solution, during which hydroxyl ions are produced. The limitation of this method is sensitive to presence of traces of acidic or basic gases in air sample (HCI and NH_3). Thus, limits the range of possible analytical applications.

Electrochemical based gas sensor operate by reacting with ozone and producing an electrical signal proportional to the ozone concentration. A typical electrochemical sensor consist of a sensing electrode (or working electrode or anode), and a counter electrode (or cathode) separated by thin layer of electrolyte. Because a current is generated in the process, the electrochemical sensor is also described as an amperometric gas sensor or a micro fuel cell. Work by Stergiou *et al*., (2009) demonstrate redox polymer electrolytes (Polyethylene oxide (PEO)/Rb/I_2 redox polymer) can be used for development of easy-constructed, cost-effective and ready-to-use sensors. However, sensor response to ozone has significant flow dependence typical of electrochemical ozone measurement (Ebeling *et al.,* 2009). Besides, the life expectancy of the electrochemical sensor is limited as it highly dependent on environmental contaminants, temperature and humidity to which the sensor is exposed.

Recently, metal oxide semiconductor based gas sensor have received much attention in ozone concentration measurement because of their simple structure, ready modification, ability to detect various gases at low concentration, easy implementation, small size and light weight. The sensor operates based on the fact that adsorption or desorption of gas molecule on the metal oxide surface leads to change in electric resistance (Belaqziz *et al.,* 2014). This change in resistance is measured electrically and is proportional to the concentration of ozone being measured. Since ozone is an oxidizing gases, n-type semiconductor where the majority charge carriers are electrons and upon interaction with ozone resulting in an increase of electrical resistance. Conversely, a p-type semiconductor with positive holes being the majority charge carriers showing a decrease of electrical resistance in the presence of ozone (Fine *et al.*, 2010). Various type of metal oxide semiconductor,

such as SnO_2, In_2O_3, ZnO, WO_3, Fe_2O_3 (Debliquy *et al.,* 2011), NiO (Demin *et al*., 2008), $SmFeO_3$ (Mori *et al.,* 2012) and In-Ga-Zn-O (Chen *et al.*, 2015) have been widely used for ozone concentration measurement.

One of the main problems associated with metal oxide semiconductor sensors is that they require operation at high temperature (Ollitrault *et al*., 2015; Rocha *et al.,* 2016), leading to high energy consumption. Work by Chen *et al.*, (2014) demonstrate Pt/TiO_2-WO_3 thick film sensor exhibits a relatively high sensitive to 2.5 ppm of ozone gas at room temperature when irradiated using 460 nm light source. However, a drawback of this sensor is long response time. The sensor based on SnO_2 thin film for efficient detection of ozone at room temperature without activation using UV radiation or catalyst has been demonstrated by Belaqziz *et al*., (2014). Disadvantage of this sensor require complex fabrication process through a heat treatment of film sensor at 300 for 1 hour. The thermal treatment at high temperature helps to improve the film density, the grain growth, the quality and the stability of the sensible material (Acuautla *et al*., 2014). On the other hand, an easy and low temperature way to prepare ozone gas sensor based on ZnO nanorods via hydrothermal process has been successfully demonstrated by Catto *et al.,* (2015). Results show ZnO nanorods display long term stability over a 6 month period at optimal temperature of 250 °C and exhibit a good sensitivity to ozone at room temperature when exposed to ultraviolet illumination. However, the sensor suffer from long response time between 40 s and 44 s and recovery varying between 9 and 11 minutes, depending on ozone concentration level.

An optical sensor based on absorption spectroscopy for ozone concentration measurement has clear advantage compared to above mentioned sensor particularly in response time. Work by Degner *et al.*, (2010) demonstrate fast response time in milisecond range for ozone concentration measurement from tenth of ppb until 100 ppm using 4 cm reflective gas cell indicates that optical measurement principle provides fast response. Basically, optical sensor based on absorption spectroscopy operates by measuring the ratio of incident and transmitted light intensity after travelling through gas cell filled with ozone. Ozone absorb light due to electronic

excitation within its molecules. For quantity analysis, Beer law is used to relate between light absorption and ozone concentration.

Ozone can absorb light at two main regions which are ultraviolet and visible region. It exhibits a strong absorption band in ultraviolet region compared to the visible region which centred at about 254 nm and 603 nm, respectively. Work by O'Keeffee *et al.*, (2007) successfully demonstrated the use of 5 cm transmissive gas cell for ozone concentration measurement based on optical absorption in the ultraviolet and visible region at 254 nm and 603 nm, respectively.

In addition, optical sensor have several advantages such as light, durable, small size, immune to electrical and electromagnetic interferences and able to remotely monitor ozone concentrations thus the control electronics can be placed away from harsh environments. By taking into account these characteristics, optical sensor are robust and highly suitable for in situ measurement as ozone is often produced in electrochemically harsh environments.

Overall, all type of gas sensor have their own advantages and disadvantages. These sensors are used to be applied in many application. Among of them, optical sensor based on absorption spectroscopy exhibit excellent performance particularly offer fast response time. Besides, optical sensor well suit to be used in harsh environment for wide range application such as detection of natural hazard ozone (Aoyagi *et al.*, 2012), and detection of ozone produced by predischarge phenomena on medium voltage (MV) electrical equipment (Maria and Bartalesi, 2012) as well as monitoring ozone concentration in the atmosphere of printing process (Yu *et al.*, 2012), food industry to prolong the shelf-life of food (O'Keeffe *et al.*, 2008) and industrial process control application (Degner *et al*., 2010).

Besides the above mentioned sensor type, there are ozone sensors using other principal of operation such as fluorescence (Felix *et al.*, 2011), thermal decomposition heat (Nakagawa *et al*., 2001) and optical sensor based on purely organic phosphor (Lee *et al.*, 2015).

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